NATIONAL BUREAU OF STANDARDS

Technical News

BULLETIN

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1901 NBS 1961

National Bureau of Standards Marks 60th Anniversary

THERMOCOUPLES PREPARED FOR CALIBRATION

U.S. DEPARTMENT OF COMMERCE — LUTHER H. HODGES, *Secretary*

NATIONAL BUREAU OF STANDARDS — A. V. ASTIN, *Director*

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COVER: Three thermocouples fused together for calibration. The wires are insulated and protected by coverings of porcelain. One thermocouple is a reference standard; the other two are being calibrated. The common junction will be inserted into an electric furnace and comparison emf readings taken at a variety of temperatures. (See "Thermocouple Calibrations," second in a series of articles on NBS measurement and calibration services, p. 44.)

NBS MARKS SIXTY YEARS

FROM THE TIME of its establishment in 1901, the National Bureau of Standards has been concerned with precision physical measurement and with the promotion of reliable and uniform measurement throughout the United States. This concern stems from the Bureau's continuing statutory responsibility for the standards of physical measurement and for providing accurate data on important properties of materials.

Although many special tasks of widely varying scope and complexity have been added to the Bureau's program over the intervening 60 years, the theme of accurate and uniform measurement has dominated its efforts.

As a Federal institution, the Bureau was established to provide essential services to the Nation's scientists and engineers in universities, industry, and other Government agencies. Scientists and engineers, individually and collectively, spearheaded efforts to establish NBS, beginning with a resolution adopted by a special commission that met at the International Electric Exhibition in Philadelphia in 1884.

It took more than a decade for this initial effort to gather momentum. But the establishment of the National Physical Laboratory in England in 1899 which in turn lagged the German Physikalisch-Technische Reichsalstalt (1887) and the Russian Central Chamber of Weights and Measures (1878, reorganized and enlarged in 1893) led to a widespread demand during the year 1900 for a similar institution in the United States. Resolutions urging the Congress to establish a national standardizing laboratory were adopted by the National Academy of Sciences, the American Philosophical Society, the American Physical Society, the American Chemical Society, and the American Institute of Electrical Engineers. Many universities, local science clubs, government engineers, and numerous individuals joined in support of the effort. The 56th Congress held hearings on the proposal during the winter of 1900–01. On March 3, 1901, the statute establishing the National Bureau of Standards became effective. The law provided for 14 employees and for erecting and equipping a new laboratory.

It is of interest on this anniversary to review some of the reasons presented as justification for the new agency. The report of the Senate Commerce Committee following its hearings carried the following statement:

"The importance of uniform standards and correct measurement, whether in the laboratory, the workshop, or in ordinary commercial transactions, is a matter so well understood that it would be a reflection upon the intelligence of any individual to offer practical illustrations or evidence of this fact, or to estimate its commercial value. Unfortunately, our knowledge of standards is often confined to the simple cases of weight, length, and capacity; but whatever may be said of correct standards or measurements in these familiar cases is equally true of all other physical quantities, many of which now enter into the operations of daily life with almost the same frequency and with the same importance as in the more common cases mentioned; for example, the measurements of temperature, pressure, light, electricity, and magnetism. In these cases the measurements are far more difficult and the instruments more complicated than those of the simpler cases, thus greatly increasing the necessity for a central standardizing bureau of authority and provided with all of the facilities necessary to secure uniformity."

The Secretary of the Treasury, in whose Department the new bureau was to be located, set forth the following argument: "Throughout our country institutions of learning, laboratories, observatories, and scientific societies are being established and are growing at a rate never equaled in the history of any nation. The work of original investigation and instruction done by these institutions requires accurate reliable standards, which in nearly every case must be procured from abroad, or can not be procured at all.

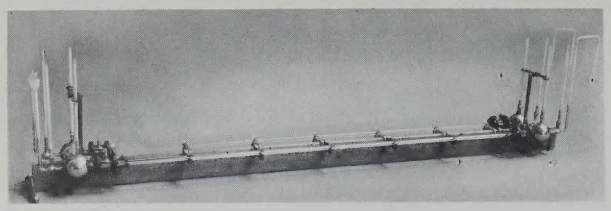
"The extension of scientific research into the realm of the extremes of length, mass, time, temperature, pressure, and other physical quantities necessitates standards of far greater range than can be obtained at present. Frequently the comparison of the same physical quantities vary with the magnitude of the quantity to be measured, and may even introduce entirely new conditions, methods, and apparatus, as in the case of high or low temperatures.

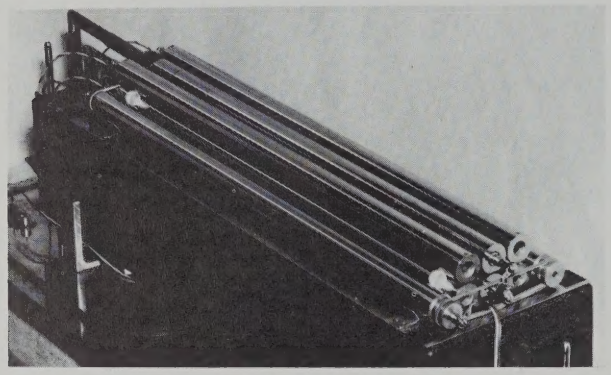
"The introduction of accurate scientific methods into manufacturing and commercial processes involves the use of a great variety of standards of far greater accuracy than formerly required. An accurate knowledge of the high temperature of a furnace or refinery, or the low temperature of a refrigerating process, is often essential to the economical working of the process.

"Enormous commercial transactions are daily based upon the reading of electrical measuring apparatus, inaccuracies of which involve great injustice and financial losses; hence the national bureau should be in a position to calibrate or test electrical standards of all kinds for commercial, as well as the most refined scientific work.

"The scientific work carried on by the different departments of the Government involves the use of many standards and instruments of precision, which are too frequently procured from abroad, owing to our own lack of facilities for standardizing.

"The manufacture of scientific apparatus and instruments of precision has been confined almost exclusively to foreign countries, but at present is growing at a rate which will soon place our own production on a par with that of any other country. In order to secure the requisite degree of uniformity and accuracy it is absolutely essential that American manufacturers of such apparatus have access to a standardizing bureau equivalent to that provided for the manufacturers of other countries, notably Germany and England.





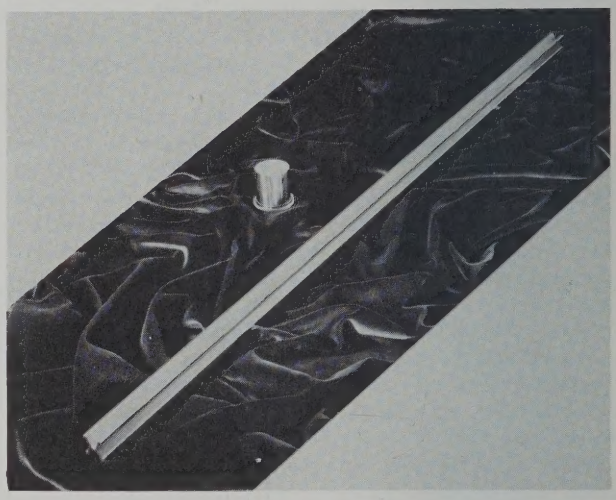
Through the years standards of measurement have changed in both physical appearance and accuracy. For example, standards of resistance: Comparisons of mercury ohm tubes (top photo) by various countries agreed to about 20 ppm in terms of the specification for such tubes about 1915. The specification, however, was in error by approximately 500 ppm in terms of the absolute ohm. Today, the calculable capacitor (bottom) is the starting point for one calculation of the ohm, now believed to be known with an error not exceeding 5 ppm.

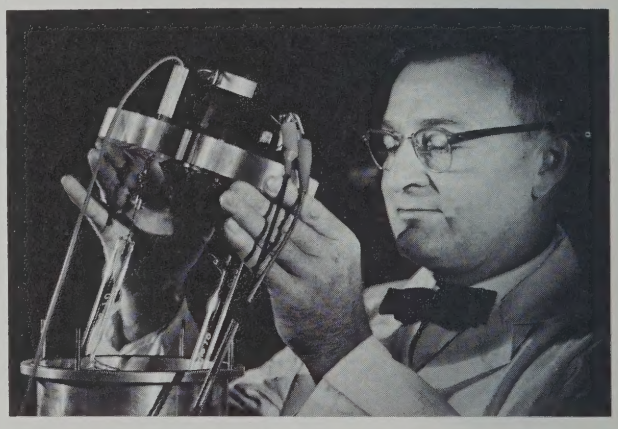
"Ample facilities should be provided for the investigation of problems which arise in connection with standards and standard measuring apparatus, since it is by the solution of these problems that the standardizing department is enabled to meet the demands of modern and improved methods of measurement."

The supporting resolution of the American Physical Society said in part: "We believe that in matters of the sort here mentioned the United States should be, if not independent of other countries, which is as impossible in science as in commerce, at least abreast of the most recent progress in any country. We therefore recommend the establishment of a laboratory possessing copies of standards of the fundamental physical quantities and capable of carrying out the most refined methods of measurement, and also of such research as shall be necessary for the further perfecting of such standards as are not yet satisfactorily fixed."

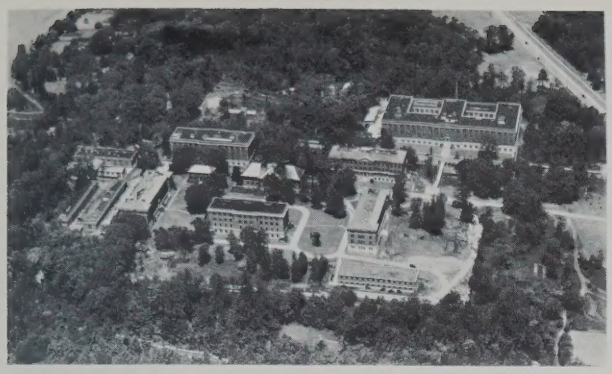
In spite of numerous achievements during its 60-year history, the NBS today finds considerable similarity between present justifications for program modifications or extension, and the initial justifications of 1900–1901. The meter is still being subdivided to smaller and smaller intervals and finer tolerances. It is still urgent to provide more accurate temperature measurements at still higher and still lower temperatures. The electrical standards have undergone an unbroken series of refinements of ever increasing difficulty, and the evolution of radio has presented a sort of continuum of new dimensions to the problem.

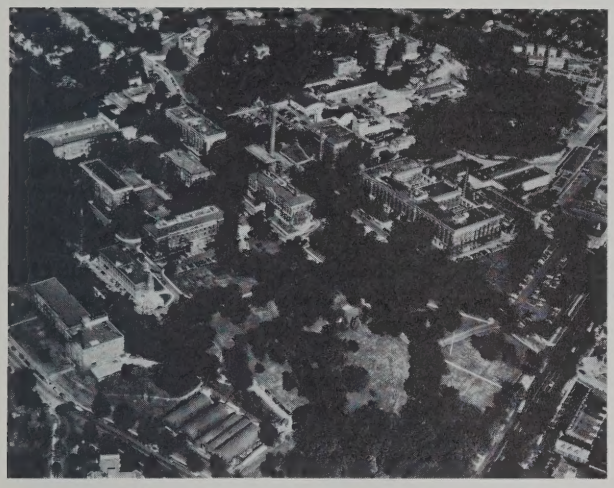
Today's measurement standards problems are the result of a growth of science and technology that completely dwarfs the rapid growth rates referred to in the early justification. The recent phenomenal growth imposes very serious problems in meeting the requirements suggested by the American Physical Society in 1900 that the laboratory should be "at least abreast of the most recent progress in any country." Although keeping abreast of the demands for urgent services in the measurement standards field appears to the present NBS management and to most of its special advisory committees a most difficult problem, there may be some comfort in the fact that similar problems have confronted the NBS before. The Bureau's first Director, Dr. Samuel W. Stratton, said in his annual report for 1916, at which time the original staff of 14 had grown to 415: "The calls upon the Bureau in connection with the scientific work of the country, and especially the industries, have grown by leaps and bounds. The Bureau is not only neglecting much work that should be

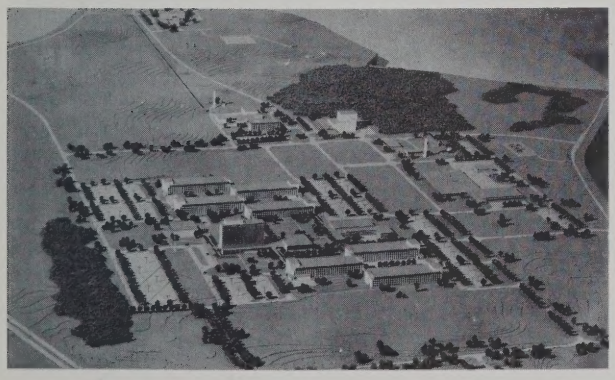




The standard of length has changed from a metal standard to the wavelength of light. When the Bureau was established in 1901, the meter bar (shown with kilogram) was the national standard of length. Today, the krypton 86 wavelength (adopted in 1960) is the international standard of length, permitting realization of the meter with an accuracy better than 1 part in 100 million.







The changing face of the Bureau: Top to bottom, NBS in 1920; a similar view today; the NBS Boulder Laboratories today; architect's model of the Bureau's new facilities soon to be constructed at Gaithersburg, Md.

done, but has been compelled to do many things in a temporary and superficial manner. This has been especially true during the past two years, nevertheless, every effort has been made to utilize the resources of the Bureau to the greatest possible extent in assisting the public to meet these new conditions. The demand on the part of the industries for accurate and reliable scientific data has never been as great or as important as at present. This demand is a rapidly increasing one.

"Never has the demand for scientific and technically trained men been as great as at present. This has resulted in the loss of many well-trained men in the Bureau's staff. The time has come when some of the salaries paid such experts must be increased or their services dispensed with. This cannot be done without a loss in quality and the deterioration of the high standard of the Bureau's work."

Almost the same words might be used in a 1961 budget justification, but with a greater sense of urgency dictated by current world conditions. The demand for better measurements standards, extended to both larger and smaller values and to increasingly extreme environmental conditions, is a problem whose growth rate has continuously accelerated over the years. In addition, the growing complexity of the Nation's technological economy puts even greater dependence on the effective interchange of data, materials, and devices, which in turn depends on effective measurement standards and accurate data on the properties of materials.

In recognition of the mounting responsibilities of NBS with the resultant dependence on specialized equipment and facilities, the Congress a few years ago authorized funds for a new site for the Bureau and for the preparation of plans and specifications for new laboratories. Funds for the first phase of construction were provided in this year's appropriation. The Bureau's 60th birthday finds it just about ready to issue an invitation for bids on the construction of the first unit at its new site. This site of 550 acres is located near Gaithersburg, Maryland, about 15 miles northwest of the present site.

The present site, consisting now of 69 acres in the heart of residential Northwest Washington, was originally a 7-acre tract. When it was occupied in 1904, its location was considered rural. With a move to a new rural location now being planned, it is of interest to read how an NBS report described its location after 10 years on the present site:

"The laboratories of the Bureau of Standards are located in the northwest section of Washington, on Pierce Mill Road, near Connecticut Avenue, and are reached by the Chevy Chase car line. It was located outside of the business center of Washington in order to insure freedom from mechanical, electrical, and other disturbances common to the business and more thickly populated sections of the city. Furthermore, the area of ground necessary precluded a site near the city. It has been found by experience that the efficiency of the employees, especially those engaged in testing and scientific investigation, has been greatly increased by the location of the laboratories in a section free from the ordinary disturbances of city life."

Joint URSI-IRE Fall 1960 Meeting

A JOINT MEETING of the International Scientific Radio Union and the Institute of Radio Engineers was held at the Boulder Laboratories of the Bureau December 12 to 14, 1960, under the chairmanship of Professor William E. Gordon of Cornell University. Five hundred and fifty attended the meeting at the invitation of the two societies to exchange technical information, coordinate research efforts, and recommend future projects.[1]

Boulder Laboratories' Alan H. Shapley, Chief of the Office of Central Radio Propagation Laboratory Liaison and Program Development, served as program coordinator and as chairman of the local arrangements committee. The meeting was held under the auspices of the International Scientific Radio Union, U.S.A. National Committee, and the Institute of Radio Engineers Professional Groups on Antennas and Propagation, Circuit Theory, Instrumentation, Information Theory, and Microwave Theory and Techniques.

URSI, named from the initials of its French title, Union Radio Scientifique Internationale, was founded in 1919 as a medium for worldwide cooperation in radio research. Besides fostering scientific discussions and exchange of ideas at the General Assemblies which meet every three years, URSI is organized into seven permanent international commissions that are continuously active. National commissions do the active work in the seven general fields.

The areas assigned to the international commissions and the chairman of each are: I—Radio Measurements and Standards, Prof. U. Adelsberger (Germany); II—Tropospheric Radio Propagation, Mr. J. Voge (France); III—Ionospheric Radio Propagation, Prof. J. A. Ratcliffe (United Kingdom); IV—Radio Noise of Terrestrial Origin, Dr. R. A. Helliwell (United States); V—Radio Astronomy, Prof. A. C. B. Lovell (United Kingdom); VI—Radio Waves and Circuits, Dr. J. Loeb (France); VII—Radio Electronics, Dr. W. G. Shepherd (United States).

The meeting began Monday morning, December 12. After a brief welcome by Dr. Frederick W. Brown, Director of the Boulder Laboratories, a combined session heard a review of the highlights of the XIII General Assembly of URSI, held in London, England, September 4 to 15, 1960. All seven international commissions were represented.

Starting Monday afternoon, simultaneous technical sessions began. During the 3 days of the meeting, 93 papers were presented relating to research by four United States commissions: 2, 3, 4, and 6.

After a banquet on Tuesday evening, December 13, Dr. J. Howard Dellinger, one of the five Honorary Presidents of URSI and former Bureau scientist, spoke on "Almost 50 Years of URSI." Following his speech, Dr. John P. Hagen of the National Space and Aeronautics Administration presented Dr. Dellinger with a citation "for long and meritorious service" to URSI.

Tropospheric Radio Propagation

At the session on refraction and absorption, a computational technique for evaluating atmospheric bending of radio waves was discussed. The effect of rain and water vapor on sky noise temperature was reported; recent measurements have indicated that during periods of rain, zenith noise temperatures can increase as much as 17 db above the usual noise background caused by oxygen and water vapor absorption. A discrepancy between theoretical predictions and actual observations of millimeter wave absorption was considered, with a postulate to account for the anomaly.

Papers on propagation measurements and theories dealt with a variety of recent investigations. Measurements of attenuation rates through certain selected elevated ducts were reported, as were measurements of fading characteristics on a knife-edge diffraction path. The geometry of several proposed scatter paths, several hundred miles long, suggests that increased relative delays of signal paths could result in significant interchannel modulation interference in an FM system; an experiment determining the amount of interference was reported. A rapid-beam swinging experiment in transhorizon propagation was the subject of another paper. Tropospheric and ionospheric scatter transmission was quantitatively explained as being the logical consequence of the average decrease in the index of refraction with height above the earth. In a discussion of median transmission loss and refractive index profile characteristics, the results of using heights other than the usual 1 km above the earth's surface were summarized.

A number of problems dealing with surface effects were presented. Examples of boundary value problems in radio wave propagation, solutions for the problem of vertical and horizontal dipoles submerged in sea water, calculations of theoretical scattering coefficient for a terrain, and a consideration of the general problem of a radiating antenna in a highly conductive medium such as the sea, were all subjects of papers. An acoustic simulator for investigating backscatter of electromagnetic waves was described.

Ionospheric Radio Propagation

The session on ionospheric propagation opened with a paper on frequency variations in vertical incidence ionospheric reflections, based on systematic recordings of the Doppler frequency shift of waves reflected from the $F2$ layer. A discussion followed concerning recordings at Palo Alto, Calif., of the instantaneous frequency of both WWV–20 and a highly stable HF transmission from Puerto Rico. Multipath propagation on transarctic HF circuits was the topic of another paper.

A number of papers were given on ionospheric disturbances. Solar-terrestrial relations and arctic radio propagation during August 1959, the influence of polar

cap absorption on HF propagation, a comparison of arctic HF transmission loss and VHF riometer data, and magnetic field micropulsations in the auroral zone, were all reported reflecting the current interest in radio transmission across the top of the world. A theoretical explanation was given for the increase of ionization associated with the geomagnetic sudden commencement. Sudden ionization anomalies in regions remote from high-altitude nuclear bursts were discussed.

Satellites and the ionosphere were the topics of another session. A discussion of detecting satellites by their influence on the ionosphere disclosed that any satellite-induced disturbance would be most detectable when directly overhead. Some relationships were derived for a satellite experiment concerned with sounding the ionosphere from above, and the results of sounding the ionosphere from a rocket were reviewed. The electron content of the ionosphere as determined from satellite Doppler data was discussed, and anomalies in the geomagnetic retardation of the spin of satellite Vanguard I were analyzed.

A number of papers on ionospheric irregularities were delivered at another session. *F*-layer irregularities, producing a phenomenon known as spread-*F*, have been observed with several different radio techniques from a number of widely separated locations on the earth's surface. A temperate latitude study of large-scale ionospheric irregularities, 100 to 400 km in horizontal extent, using satellite transmissions was also reported. Conclusions were that these large irregularities are primarily a daytime phenomenon, and occur on about one-third of all days. Observations of these irregularities are in general agreement with the results obtained from various reflection experiments, and, in addition, suggest that the irregularities extend above the level of maximum electron density.

Radio Noise of Terrestrial Origin

A session on atmospheric noise opened with a discussion of radio noise generated by a tornado oscillator. Such an oscillator is characterized by a complete absence of radio frequencies below 75 kc/s and a noticeable increase in high frequencies as the tornado itself begins to form. A description was given of a seagoing lightning generator and how the personnel of this laboratory vessel uses the known characteristics of lightning pulses to study atmospheric propagation. Another paper was devoted to instrumentation for recording spectrum occupancy and radio noise levels from 0 to 600 kc/s. An account was given of the prediction of atmospheric noise levels from thunderstorm counts.

The subjects of another session, VLF and whistler mode propagation, were concerned with special aspects of radio noise propagation. Propagation attenuation rates at ELF, observations of low-frequency fields and propagation characteristics in arctic regions, daytime phase characteristics in the VLF band, and VLF phase perturbation associated with meteor shower ionization were discussed. A mode theory of ionic duct propagation was presented; this theory has been used to investigate propagation through the exosphere along the lines of flux of the earth's magnetic field, and results in a better understanding of whistler mode propagation.

Radio Waves and Circuits

At the session on surface waves, a paper presented a new method for analyzing the far zone radiation of an antenna with a modulated aperture field. Another paper outlined a general principle of wide-band matching of impedances using active networks, and included a description of an experimental verification of the technique where a load was matched to a generator with a purely resistive internal impedance.

A session was devoted to information- and circuit-theoretic problems in space probing and communication. Papers were presented on interplanetary communications systems for distances of 100 million miles or more, use of the LASER for space communications, and surface-to-surface communications by means of the Echo satellite.

A session was held on information and radio circuit theories. One paper was primarily concerned with the entropy loss in a communications channel as a result of EM propagation through turbulent regions with space-time random dielectric constant. A multipath propagation problem was discussed, showing that a solution can be derived from a class of linear differential equations with random coefficients. Some general questions dealt with information rates through a channel consisting of a photon source, an amplifier, and a photon detector. A design theory for optimum negative resistance amplifiers was reviewed, and bandpass measurements of a lunar reflection circuit were reported.

The session on antennas included both antenna system design and theory. The design of a high-resolution electronically scanned antenna array was reported. Design problems of the UHF, high-power line source feed for the Air Force's 1,000-ft spherical reflector were disclosed. Antenna arrays with variable interelement spacing were also described. On the theoretical side, the development of antenna patterns for maximum information transmission rates under simple multipath conditions was surveyed, and a paper was presented on basic theorems derived from considerations of optimum spherical and cylindrical arrays.

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[1] *Because of the large number of papers presented and the extent of the discussions at the meetings, this account could mention only some of the highlights. Abstracts of the papers were printed in the program. As the U.S.A. National Committee does not plan to publish proceedings, those wishing copies of the papers should obtain them through the authors. A complete list of registrants is available from Mrs. Helen Hart, U.S.A. National Committee, National Academy of Sciences-National Research Council, 2101 Constitution Ave. NW., Washington 25, D.C.*

Determination of Copolymer Composition

THE BUREAU, under the sponsorship of the Government Synthetic Rubber Program, has developed a precise procedure for determining copolymer composition.[1] This method, in which the sample is burned to produce water and carbon dioxide, has been used to measure the ratio of bound styrene to butadiene in samples of synthetic rubber. Other copolymers containing monomers differing significantly in carbon-hydrogen ratio could be analyzed with little modification of the present procedure.

A need for the determination of copolymer composition arose as part of an investigation of natural and synthetic rubbers. To perform this analysis, L. A. Wood, I. Madorsky, and R. A. Paulson adapted a method previously developed for the determination of carbon and hydrogen in hydrocarbons.[2] Although the new procedure is precise, it is too time consuming to be of value in routine copolymer determinations. However, it has been used to measure the copolymer composition of reference standards, which then serve as the basis for the development of more rapid techniques.

The copolymer must be highly purified before the composition is determined. Purification is accomplished by dissolving the sample in benzene, followed by coagulation with methyl alcohol. This process, repeated three times, eliminates fatty acids and their salts, stabilizer, and low-molecular-weight polymer. The spongy mass of polymer formed during purification is stored in a vacuum desiccator at low temperature until analysis is performed.

Portions of the purified copolymer are analyzed for carbon and hydrogen content in a combustion train. A weighed sample is placed in a Pyrex test tube capped with platinum gauze, which in turn is placed in the quartz combustion tube of the analytical apparatus. The sample is heated in an electric furnace, and the combustion products are carried away by a continuous flow of purified oxygen. Water formed during the combustion is collected in a tube packed with magnesium perchlorate and phosphorus pentoxide. The carbon dioxide is absorbed in a second tube containing soda asbestos, magnesium perchlorate, and phosphorus pentoxide. After 7 hours' flushing, the absorption tubes are removed from the apparatus and carefully weighed to determine the amounts of carbon dioxide and water collected. From the known weight of the sample, and the weights of the combustion products, the ratio of copolymer constituents can be calculated.

In the analysis of a copolymer containing styrene (C_8H_8) and butadiene (C_4H_6), the percentage of styrene by weight (X) is given by the expression

$$X=29.0831[11.1809-100/(R+1)],$$

in which R represents the carbon-hydrogen ratio from the analysis. The constants are derived from the molecular formulas of the polymers and the atomic weights of carbon and hydrogen.

The results of many determinations show this method to be extremely precise. Analysis of many copolymers, ranging from 8.6 to 83.7 percent styrene, gave a mean standard deviation of 0.0010. This corresponds to a standard deviation of about 0.036 percent bound styrene for polymers of low styrene content and 0.018 percent for polymers of high styrene content. The accuracy of the method is demonstrated by the fact that observations of carbon-hydrogen ratio for four out of five samples of polybutadiene differed by less than one standard deviation from the theoretical value calculated from its known composition.

Margaret Hines weighs an absorption tube (left) to determine the amount of carbon dioxide formed when a styrene-butadiene copolymer was burned. An equal-volume counterpoise is placed to the right to compensate for buoyancy effects. From the amount of carbon dioxide and water (absorbed in another tube) formed when a known amount of copolymer is burned, the ratio of the two constituents can be accurately determined.

Minor amounts of impurities containing no carbon or hydrogen can be tolerated in this analysis, as they will not affect the carbon-hydrogen ratio. However, bound mercaptans (compounds containing carbon, hydrogen, and sulfur), used as modifiers in the polymerization of the styrene-butadiene rubbers, do contribute small amounts of carbon and hydrogen to the reaction products. To compensate for this interference a sulfur analysis is run on another portion of the material being tested, and from the result a correction factor is calculated.

Samples whose copolymer composition had been determined by this process were used as reference

standards for refractive index measurements. Tables were prepared that related copolymer composition—known from combustion analysis—to an accurately determined refractive index. Analysis of butadiene-styrene copolymers can now be made on a rapid routine basis, using the simple refractive index measurement.

[1] *For further details, see* Determination of copolymer composition by combustion for carbon and hydrogen, *by L. A. Wood, I. Madorsky, R. A. Paulson, J. Research NBS* **64A**, *157–162 (March–April 1960).*

[2] Note on the macroanalysis of carbon and hydrogen by combustion, *by D. D. Wagman and F. D. Rossini, J. Research NBS* **32**, *95 (1944) RP1577.*

Recalibration of Standard Thermal Neutron Flux

THE VALUE of the standard thermal neutron flux maintained by the Bureau has been changed as the result of a recent gold foil recalibration.[1] The new value, 4,203 neutrons/cm^2–sec, is a weighted average of the gold determination and a previous value based on the cross section of boron.[2]

The standard neutron flux provides a basis against which other neutron fluxes can be calibrated. This is normally done by irradiating gold foils submitted by laboratories engaged in neutron research. The activity of the irradiated foils, after exposure to the standard flux, is then determined by the user. From the measured activity of the standard-irradiated foils, a factor relating thermal neutron flux to foil activity can be determined. This factor permits the foils to be used in the calibration of unknown fluxes.

Because of an increased demand for the calibration of unknown neutron fluxes by foil activation, E. R. Mosburg and W. M. Murphey recalibrated the standard flux so that the value would be independent of the original boron determination. Accurate calibration of the flux in terms of gold was made possible by the increased precision of a redetermination of the thermal cross section of gold.[3]

Neutrons are produced in the Bureau's standard flux by the action of α-particles—resulting from radium decay—on beryllium. To recalibrate the flux, thin gold foils (0.001 and 0.00025 in.) were exposed to it for several half-lives (half-life of $_{79}Au^{198}$ is 2.7 days). The activity of the irradiated gold was then determined in a β-γ coincidence counter. The foil was placed between concentric cylinders of a plastic scintillator, which reacted to β-radiation. γ-rays resulting from the excited state of mercury ($_{79}Au^{198} \rightarrow {}_{80}Hg^{198} + \beta$) were detected by a well-type sodium iodide (thallium-activated) scintillator which surrounded the plastic assembly. A thin-layer of aluminum or cadmium was placed over the plastic scintillator to prevent 1-Mev electrons from entering the iodide crystal. Flashes from the scintillators were detected by photomultipliers, the pulses from which were applied to linear amplifiers.

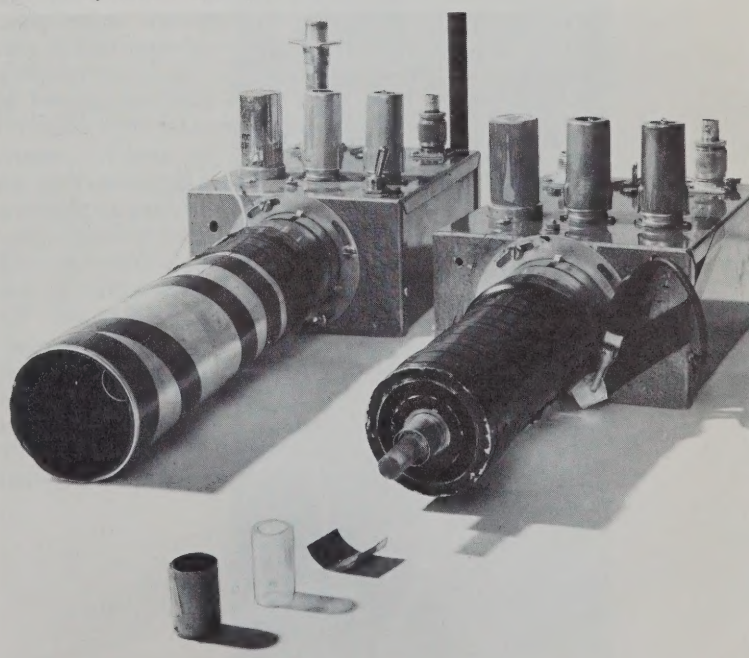
Adequate shielding was required to permit accurate counting of the γ-radiation. The scintillation assembly was therefore surrounded by a 4-in. lead and 1-in. mercury barrier. This protection reduced the background-to-gold count ratio to 0.03.

The absolute decay rate of each set of foils was based on a series of 15-min counts taken over a period of several days. The flux value based on gold, after calculation of all errors and corrections, was weighted and averaged with the boron figure, to give a new value of 4,203 neutrons/cm^2-sec. As radium decay progresses, this figure must be corrected to compensate for the growth of $_{84}Po^{210}$, which also emits α-particles.

[1] *For further details, see* A recalibration of the NBS standard thermal neutron flux geometry, *by E. R. Mosburg, Jr. and W. M. Murphey, J. Nuclear Energy (to be published).*

[2] Absolute calibration of the NBS standard thermal neutron density, *by J. A. DeJuren and H. Rosenwasser, J. Research NBS* **52**, *93 (1954) RP2477.*

[3] *Gould, Taylor, Rustad, Melkonian, and Havens, Bul. Am. Phys. Soc. II* **2** *42 (1957).*



Counting apparatus used in a recent recalibration of the standard thermal neutron flux. The thin gold foil is exposed to the standard neutron flux for several days, and then is placed between the concentric cylinders of a plastic scintillator which is sensitive to β-rays. The right-hand assembly fits inside the tube at the left, which contains a sodium iodide scintillator for the detection of γ-rays. An aluminum or cadmium cap (foreground) is placed over the plastic to prevent β-rays from entering the crystal.

March 1961

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THERMOCOUPLE CALIBRATION

Second in a Series on NBS Measurement and Calibration Services

THERMOCOUPLES are calibrated by the Bureau over the temperature range of −190 to +1,100 °C.[1] This service, performed for reference standards laboratories, industrial concerns, and various research groups, plays an important role in providing more accurate temperature determinations on all levels. Modern technology, through its need for temperature measurements of greater accuracy, has increased the importance of a uniform system of measurement. The Bureau, by maintaining the standards against which temperature measuring devices are calibrated, insures a common basis for temperature measurement in this country.

The Bureau also provides other allied services in the area of thermocouple calibration. Thermocouple materials—wires of various compositions—are calibrated to determine the voltages they produce when fused to a standard platinum wire. Occasionally, the accuracy of a potentiometer used in thermoelectric measurements will be determined. Samples of freezing point standards—aluminum, copper, lead, zinc, and tin—are available to the public on a fee basis.[2] These standards provide fixed points against which thermocouples can be calibrated in outside laboratories.

A thermocouple, in its commonly used form, consists of a pair of wires of dissimilar metals joined together at one end to form a measuring junction. The other ends are connected to lead wires which are in turn connected to a sensitive voltage measuring device. The electromotive force (emf) produced in such a system depends upon the composition of the wires used, and the difference in temperature between the two junctions. By determining the emf-temperature relationship of a particular thermocouple at several known points, temperature measurements of considerable accuracy can be made within the bounds of the calibration and, with some loss of accuracy, in extrapolated regions.

Various combinations of materials are employed to make useful thermocouples. Because of their superior stability at high temperatures, platinum versus platinum-10-percent-rhodium thermocouples are widely used over the range of 0 to 1,450 °C. At lower temperatures, however, this combination produces an emf so small as to make accurate measurement very difficult.[3]

Base metal thermocouples can be used to measure temperatures as low as −190 °C. However, they are usually not as stable at high temperatures as platinum thermocouples. Examples of base metal thermocouples, with their useful temperature ranges, include Chromel-Alumel (−190 to 1,100 °C.), iron-constantan (−190 to 760 °C) and copper-constantan (−190 to 300 °C).

The calibration procedure followed by the Bureau [4] depends upon the type of thermocouple submitted, and the accuracy-and-range requirements of the user. Base metal thermocouples are compared with a platinum resistance thermometer over the range of −190 to 538 °C. They are also compared with a standard

Type of thermocouple	Methods of calibration	Temperature range
		°C
Platinum versus platinum-10-percent-rhodium.	International Temperature Scale (fixed points).	630.5 to 1,063.
Platinum versus platinum-rhodium.[a]	Fixed points	0 to 1,450
	NBS Standard Samples, fixed points.	0 to 1,450
	Comparison with standard thermocouple.	0 to 1,450
	do	0 to 1,450
Chromel-Alumel	Comparison with standard thermocouple.[a]	0 to 1,100
	do	0 to 1,100
	Comparison with standard resistance thermometer [b] or at fixed points.	0 to 350
	Comparison with standard resistance thermometer.[b]	0 to −190
Iron-constantan	Comparison with standard thermocouple.[a]	0 to 760
	do	0 to 760
	Comparison with standard resistance thermometer [b] or at fixed points.	0 to 350
	Comparison with standard resistance thermometer.[b]	0 to −190
Copper-constantan	Comparison with standard resistance thermometer [b] or at fixed points.	0 to 300
	Comparison with standard resistance thermometer.[b]	0 to 100
	Fixed points	0 to 100
	Comparison with standard resistance thermometer.[b]	0 to −190
	Fixed points	0 to −190

[a] Either 10- or 13-percent rhodium. [b] In stirred liquid bath.

platinum versus platinum-10-percent-rhodium thermocouple, maintained by the Bureau, up to 1,100 °C. Platinum thermocouples are compared with the standard thermocouple, or, if greater accuracy is required, the emf developed at fixed points on the International Practical Temperature Scale is determined.

Because the emf developed by a particular thermocouple depends upon the temperature difference between the two junctions, all calibrations at the Bureau are performed with a reference-junction temperature of 0 °C. This eliminates the need for correcting for constantly changing room temperature. The thermocouple wires are connected to lead wires, usually by immersion in mercury, and the connection is maintained at 0 °C in a Dewar filled with ice and water.

Annealing

The calibration of any platinum thermocouple or test wire is preceded by annealing at 1,450 °C for 1 hr. Mechanical strains are relieved by this procedure, and the effect of surface impurities may be minimized.

Left: Base metal thermocouples are calibrated to temperatures as low as —190 °C. Here, Mrs. Minnie Massie checks the platinum resistance thermometer used to determine the bath temperature. This bath contains liquid nitrogen. Below, right: All platinum thermocouples are annealed prior to calibration. The wires, suspended in a metal cabinet, are heated to 1,450 °C for 1 hr. This treatment helps to remove any strains present in the metal and may remove surface impurities.

Base metal thermocouples are not annealed, as they are less stable at high temperatures, nor are they calibrated against fixed points.

Annealing is accomplished by passing a current through the thermocouple while it is suspended between two electrodes. The suspension is done in such a manner as to keep tension and stretching to a minimum. The temperature of the wire is conveniently determined with an optical pyrometer.

Fixed Point Calibration

When a calibration of maximum accuracy is required, the temperature-emf relationship of platinum versus platinum-rhodium thermocouples is determined at four fixed points on the International Practical Temperature Scale.[5] This scale, adopted by international agreement in 1927 and revised in 1948 and 1960, is based upon a series of fixed and reproducible temperatures, and upon specified formulas for the relations between temperature and the indications of the instruments calibrated at these fixed points. The points used by the Bureau in the thermocouple calibrations are the freezing points of gold (1,063 °C), silver (960.8 °C), antimony (630.5 °C), and zinc (419.5 °C).

Extremely pure gold and silver must be used in freezing point determinations, for as little as 0.05 percent impurity may lower the freezing temperature by 0.1 °C. The purified metal is melted in a cylindrical graphite crucible positioned within an electric furnace. To avoid oxidation, the silver is covered with a layer of graphite. The thermocouple, protected by a closed-end

Calibration points	Accuracy at observed points	Method of interpolating	Uncertainty in interpolated values
	°C		°C
reezing point of Sb, Ag, and Au	0.2	Equation: $E=a+bt+ct^2$	0.3
reezing point of Zn, Sb, Ag, and Au.	.2	Difference curve from reference table	0.5 to 1,100 and 2 at 1,450.
reezing point of Sn, Zn, Al, and Cu.	.2	do	.5 to 1,100 and 2 at 1,450.
bout every 100° C	.3	do	.5 to 1,100 and 2 at 1,450.
bout 600° and 1,100° C (or more points).	.3	do	1 to 1,100 and 3 at 1,450.
bout every 100° C	.5	Linear	1
bout 500°, 800°, and 1,100° C (or more points).	.5	Difference curve from reference table	2
bout every 100° C	.1	do	0.5
bout every 50° C	.1	do	.5
bout every 100° C	.5	Linear	1
bout 100°, 300°, 500°, and 750° C	.5	Difference curve from reference table	1
bout every 100° C	.1	do	0.5
bout every 60° C	.1	do	.5
bout every 100° C	.1	Equation: $e=at+bt^2+ct^3$ or difference curve from reference table.	.2
bout 50° and 100° C	.05	Equation: $e=at+bt^2$ or difference curve from reference table.	.1
oiling point of water	.05	Equation: $e=at+0.04t^2$	.2
bout every 60° C	.1	Equation: $e=at+bt^2+ct^3$ or difference curve from reference table.	.2
ublimation point of CO_2 and boiling point of O_2.	.1	Difference curve from reference table	.3

Control panel for thermocouple calibration. Platinum thermocouples are calibrated against platinum resistance thermometers at 419.5 °C and 630.5 °C. The thermocouple and the resistance thermometer are placed in a copper-block comparator inside an electric furnace. George Burns (left) and John Evans take simultaneous readings of emf and resistance, which are repeated at 30-sec intervals. The upper portion of the panel contains the furnace control equipment.

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porcelain tube, is immersed in the molten metal to a depth of at least 10 cm. Electromotive force readings, determined with a sensitive potentiometer, are taken at 30-sec intervals during the cooling of the metal. The constant emf, corresponding to the freezing portion of the cooling curve, is then reported.

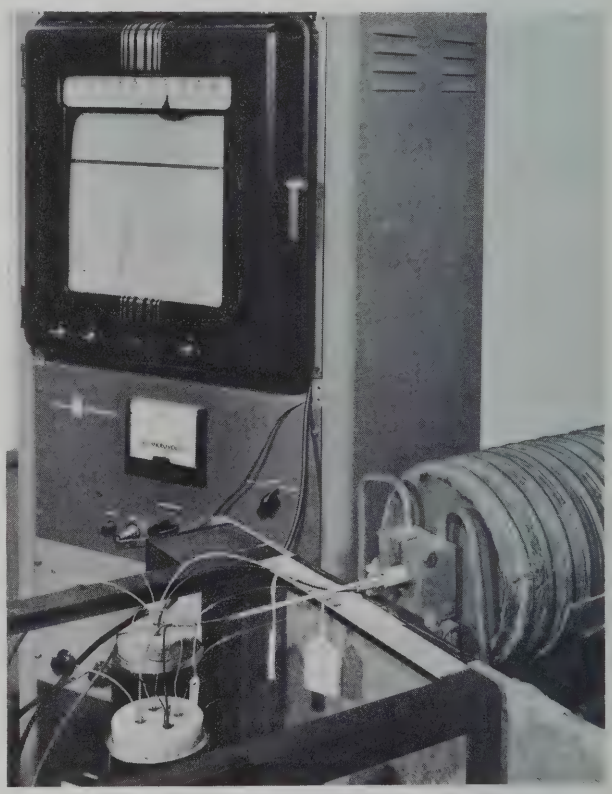
As the International Practical Temperature Scale is defined up to 630.5 °C with a platinum resistance thermometer, themocouples are calibrated against a resistance thermometer at the zinc and antimony points. This comparison is carried out in a copper-block comparator heated in an electric furnace. The block temperature is accurately determined by a platinum resistance thermometer, which is positioned as near as possible to the junction of the thermocouple. The furnace is regulated by an automatic control system, which maintains the temperature in the region of the thermocouple junction to ± 0.01 °C. When a temperature corresponding to the freezing point of zinc or antimony is approached, simultaneous readings of thermometer resistance and thermocouple emf are taken at 30-sec intervals. The emf corresponding to the fixed point, as determined by the resistance thermometer, is then reported.

An equation that will allow interpolation between 630.5 and 1,063 °C is calculated from the observed data. For temperatures outside of this range, a curve may be plotted relating observed emf to the difference in emf between a reference table and the test thermocouple. Such a curve results in extrapolated values of high accuracy below the zinc point, and values of lesser accuracy above the gold point.

Comparison Calibration

The comparison of base metal and platinum thermocouples with the standard platinum versus platinum-10-percent-rhodium thermocouple maintained by the Bureau is performed over the range of 50 to 1,100 °C. When individual thermocouple wires are being tested, one or more of the test wires are fused to a length of the standard platinum wire, and a standard platinum thermocouple is fused to this junction to provide a basis for comparison. When complete thermocouples are being tested, a common junction is made between one or more test thermocouples and the standard thermocouple. The bundle of thermocouples, each insulated by a length of 2-hole porcelain tubing which covers all but the fused junction and enough wire to reach the reference junction, is inserted into a closed-end porcelain protection tube, which is placed in an electrically heated tube furnace. The emf of the standard and each test wire or thermocouple is determined at a number of preselected temperatures, usually at intervals of 100 °C.

When more than four thermocouples are run concurrently, the respective emf's are determined man-



Apparatus used for thermocouple calibration from 50 to 1,100 °C. A bundle of several thermocouples is heated in an electric furnace (right), and the reference junctions are maintained at 0 °C in an ice-filled Dewar (lower left). As the temperature increases, the strip-chart recording instrument produces a continuous record of emf values for each thermocouple.

ually through the use of two potentiometers, one which measures the emf of the standard and one which measured each test thermocouple individually. If no more than four thermocouples are run at one time, a semiautomatic thermocouple comparator is used. This device records the emf difference between each thermocouple and the standard on a strip chart as a function of temperature, as determined by the standard thermocouple.

Calibration in Liquid Baths

When base metal thermocouples are to be calibrated at low temperatures, they are compared with platinum resistance thermometers in a variety of liquid media. In all cases, the thermocouple being calibrated is inserted in a relatively close fitting glass protection tube and placed in a liquid bath side-by-side with a platinum resistance thermometer. The liquid is stirred or agitated to insure uniformity of temperature in the measuring region.

At the lower limit of calibration, about −190 °C, the thermocouple is placed in an open Dewar filled with liquid nitrogen. Gaseous nitrogen is bubbled through to stir the fluid. At a slightly higher temperature, approximately −183 °C., liquid oxygen is used in place of liquid nitrogen. Commercial gaseous oxygen is liquefied shortly before use by passing through a copper coil submerged in commercially prepared liquid nitrogen.

Liquid oxygen is prepared at the Bureau for use in low-temperature thermocouple calibrations. Here gaseous oxygen is circulated through a copper coil immersed in a liquid-nitrogen-filled Dewar flask. The liquid oxygen is collected in a second flask.

From −140 °C to slightly below 0 °C an automatically controlled cryostat [6] is used to provide a variety of temperatures. The bath, cooled by liquid nitrogen, is filled with a mixture of carbon tetrachloride (49.4 wt.%) and chloroform (50.6 wt. %) for temperatures down to −75 °C. For temperatures down to −140 °C., a mixture of chloroform (14.5%), methylene chloride (25.3%), ethyl bromide (33.4%) *trans*-dichloroethylene (10.4%), and trichloroethylene (16.4%) is used.

At 0 °C all test thermocouples produce no emf, as the reference junction is also maintained at 0 °C. For values slightly above 0 °C to just below the boiling point, water is used as the heating liquid.

Comparison measurements over the range of 100 to 300 °C are made in two different oil baths, one used between 100 and 200 °C and the other from 200 to 300 °C.[7] Such factors as viscosity and flash point determine the usefulness of a particular oil bath. A stirred bath of liquid tin is used for temperatures up to 538 °C, the upper limit of the liquid-bath technique.

Accuracy

The accuracy of a particular calibration depends upon the material being tested, the type of calibration made (fixed point or comparison), and the range over which a temperature-emf relationship is established. Accuracies range from 0.05 °C for a copper-constantan thermocouple compared with a standard resistance thermometer to 0.5 °C for a Chromel-Alumel thermocouple compared against a standard thermocouple. Of course, the uncertainty of interpolated values is greater than that at fixed points, and this uncertainty increases as the difference from the nearest known point increases (see table).

A certificate is prepared and sent to the user for each thermocouple that is calibrated. This certificate lists the emf developed by the thermocouple over a specified range of temperatures. If the thermocouple is of platinum versus platinum-10-percent-rhodium and has been calibrated against fixed points, the equation for interpolation between 630.5 and 1,063 °C is also given.

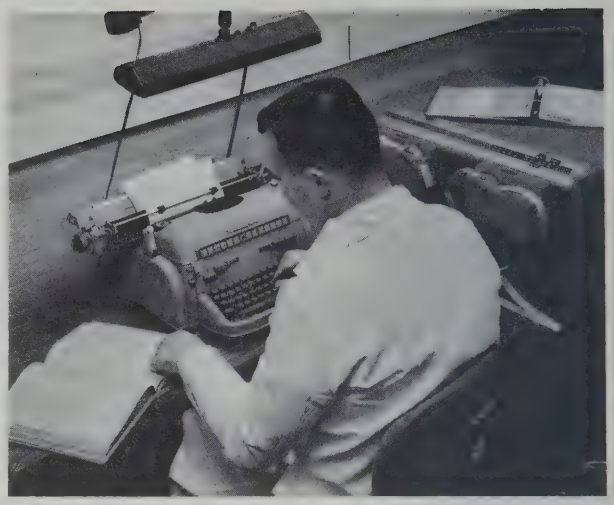
Thermocouple Research

The Bureau is conducting a variety of research programs designed to increase the useful range of thermocouples, and to improve upon the procedures used in present calibrations.

Experiments with a number of combinations, including iridium versus iridium-rhodium, tungsten versus rhenium, and others, may eventually extend the upper limit of thermocouple measurements to above 2,000 °C. A furnace is being constructed that will provide accurate temperature control above 2,000 °C. At extremely low temperatures, down to 4 °K, such metals as gold-cobalt and silver-gold are being tested against copper magnet wire.

At present, the semiautomatic comparator can be used only when platinum thermocouples are compared

A punched-tape operated typewriter is used to prepare thermocouple calibration certificates. George Burns types in the data.



with the platinum standard. Future developments may extend the range of this device so that base metal-versus-platinum comparisons can be made.

Equipment is being designed that will place the fixed-point calibration procedure on an almost automatic basis. Potentiometer and resistance readings will be recorded on punched tape, and converted to temperature-emf relationships with a computer. The results will be recorded on a magnetic tape, which will automatically print calibration tables. A tape-typewriter system is currently being used to type the certificates, but temperature-emf values must now be inserted by hand.

[1] Test fee schedules of the National Bureau of Standards, *p. 17, (1959). Available from the Office of Technical Information, National Bureau of Standards, Washington 25, D.C.*

Copies of 2, 3, 4, 5, and 7 below may be ordered from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C.

[2] Standard materials issued by the National Bureau of Standards, *NBS Circ. 552 (35 cents)*.

[3] Reference tables for thermocouples, *NBS Circ. 561 (55 cents)*.

[4] Methods of testing thermocouples and thermocouple materials, *NBS Circ. 590 (20 cents)*.

[5] The International Practical Temperature Scale of 1948, *by J. F. Stimson, J. Research NBS* **65A,** 139 (1961).

[6] Temperature, its measurement and control in science and industry, **1,** 206 (Reinhold Pub. Corp., New York, N.Y., 1941).

[7] Calibration of liquid-in-glass thermometers, *NBS Circ. 600 (20 cents)*.

Radiation Field from a Rectangular Source

A SERIES-EXPANSION METHOD for calculating the radiation received by a detector from a rectangular source has been developed by the Bureau [1] with support from the Office of Civil and Defense Mobilization, the Navy Bureau of Yards and Docks, and the Defense Atomic Support Agency. Although developed primarily for use in problems of shielding against gamma radiation, this method has potential applications in other problems involving rectangular sources of radiation, such as occur in photometry and food irradiation.

The penetration of radiation into structures has been the subject of a general program of theoretical [2,3] and experimental [4] investigations at the Bureau and other Government agencies, as well as at privately operated laboratories. The theoretical investigations involve (*a*) a determination of the angular distribution of the radiation that emerges from the surface of the source, and (*b*) a calculation of detector response, i.e., a quantity proportional to the total amount of radiation received by the detector from all parts of the source surface.

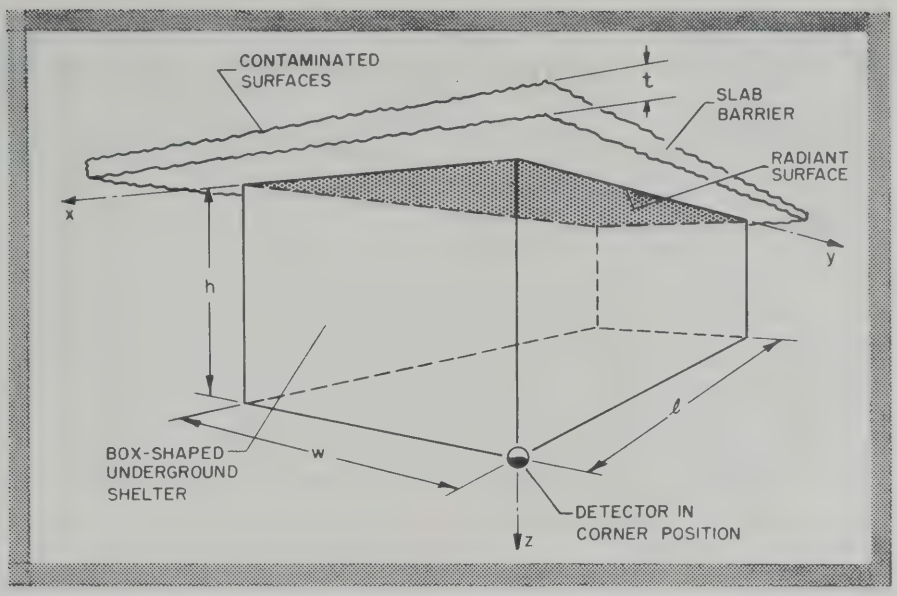
Earlier investigations at the Bureau contributed much information concerning the angular distributions [5] in addition to a procedure for obtaining the detector response by utilizing circular-sector approximations to rectangular source shapes.[3] The present method, which draws to some extent upon similar treatments in illumination [6] and heat-exchange [7] engineering, was developed by J. H. Hubbell, R. L. Bach, and J. C. Lamkin, and is based in part on initial exploratory work by Berger and Lamkin.[2]

The method utilizes information on the angular distribution in the form of coefficients of a Legendre expansion, and determines the detector response as a sum of products of these coefficients and other coefficients characteristic of a particular source rectangle. The resulting sum is accurate provided that either source angular distribution or source rectangle can be described by only a small number of coefficients.

Alternative sums are utilized for cases in which the sum described is not sufficiently accurate. These alternative sums represent the angular distribution of the source as a secant power series rather than a Legendre expansion.

The two types of geometrical coefficients generated and utilized in this investigation are valid for any angular distribution and any radiation type.

A similar investigation is now in progress with the object of calculating the radiation which an off-axis detector receives from a circular disk source. An example of such a calculation would be the estimation of the neutron flux around the face of a cylindrical thermal column of a research reactor.



Underground shelter with a detector at distance h below one corner of a radiating rectangular ceiling of width w and length l. The angular distribution $g(\theta)$ of radiation at the barrier exit (radiant) surface ($z=0$) is dependent upon (a) the species distribution of radioisotopes on the contaminated surface, (b) the attenuation properties of the slab barrier, and (c) the barrier thickness t.

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[1] *For further details, see* Radiation field from a rectangular source, *by J. H. Hubbell, R. L. Bach, and J. C. Lamkin, J. Research NBS* **64C**, *No. 2, 121–138 (1960).*

[2] Sample calculations of gamma-ray penetration into shelters: contributions of sky shine and roof contamination, *by M. J. Berger and J. C. Lamkin, J. Research NBS* **60**, *109 (1958) RP2827.*

[3] Structure shielding against fallout radiation from nuclear weapons, *by L. V. Spencer, NBS Mono. (to be published).*

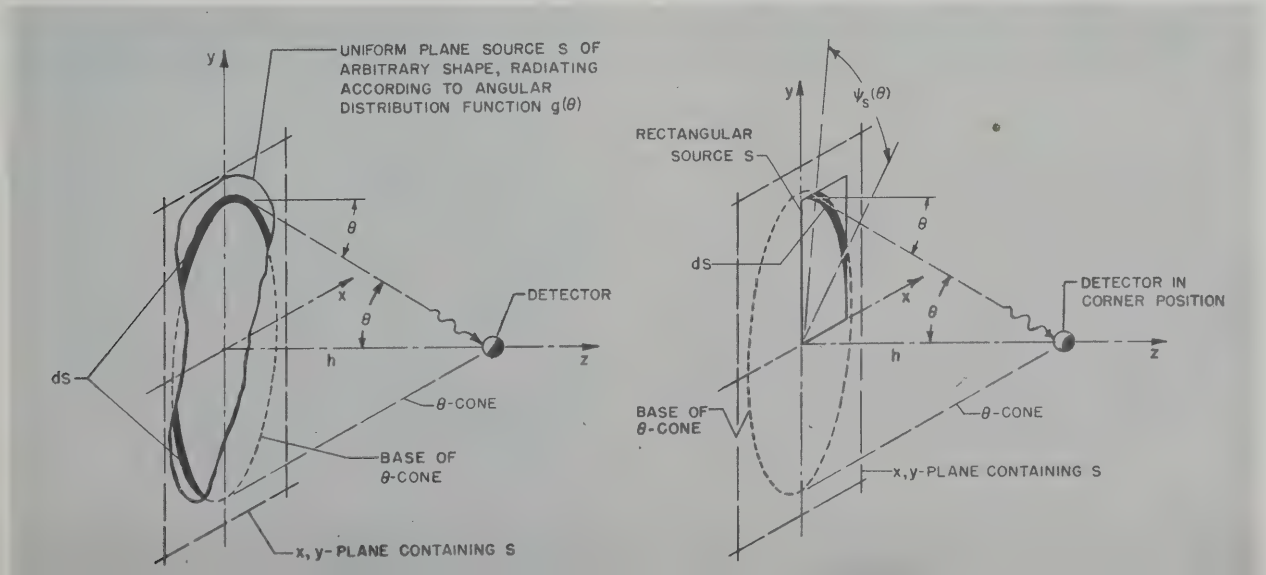
[4] Experimental evaluation of the radiation protection afforded by residential structures against distributed sources, *by J. A. Auxier, J. O. Buchanan, C. Eisenhauer, and H. E. Menker, CEX 58.1, ORNL (Jan. 19, 1959).*

[5] Penetration and diffusion of X-rays, *by U. Fano, L. V. Spencer, and M. J. Berger, Encyclopedia of Physics (Springer-Verlag, 38 II, 1959).*

[6] A treatise on geometrical optics, *by R. A. Herman, p. 210 (Cambridge Univ. Press, London, 1900)*; Geometrical calculation of illumination due to light from luminous sources of simple forms, *by Z. Yamanouti, Researches Electrotech. Lab. (Tokyo), No. 148 (1924)*; Light distribution from rectangular sources, *by P. Moon and D. E. Spencer, J. Franklin Inst.* **241**, *195 (1946)*; Radiation characteristics of semicircular, circular and rectangular surface sources, *by A. I. Mahan and W. F. Malmborg, J. Optical Soc. Am.* **44**, *644 (1954).*

[7] Die Wärmeaufnahme der bestrahlten Kesselheizfläche, *by O. Seiber, Arch. Wärmwirtsch.* **9**, *180 (1928).*

Left: Geometrical schematization of the general plane-source problem. The θ-cone is the cone of radiation received by the detector at angles between θ and $\theta+d\theta$ with respect to the z-axis. This radiation emerges from a differential source area element dS which comprises a portion (or portions, as this example) of the base of this θ-cone in the x,y-plane. The total radiation received by the detector is the sum of contributions from all such dS elements, each weighted by the angular distribution function $g(\theta)$ which characterizes the emitting surface. Right: Situation when the plane source S is a rectangle with the detector opposite a corner. The azimuthal angle $\psi_S(\theta)$ is called the "angular response function."



STANDARD MATERIALS

Metallo-Organic Standard Samples

A GROUP of 24 metallo-organic standard samples, intended for use in preparing lubricating oil solutions containing known amounts of the elements, is now available. These stable, oil-soluble substances are designed for spectroscopic analysis, but are suitable for other analyses. Prepared in crystalline form for easy weighing and handling, they may be purchased for $6.00 per 5-g unit of material.

Standard samples containing the following elements are now available: Aluminum, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, nickel, phosphorus, potassium, silicon, silver, sodium, strontium, tin, vanadium, and zinc. All except six of these elements are incorporated in the form of the metal salt of cyclohexanebutyric acid. The other elements are dispensed as menthyl borate, tris(2-hydroxyacetophenono) chromium-III, triphenyl phosphate, octaphenylcyclotetrasiloxane, dibutyltin bis(2-ethylhexanoate), and bis(1-phenyl-1, 3-butanediono)oxovanadium-IV.

A certificate of analysis, plus directions for preparing a solution of the substance, is distributed with each sample. Orders should be directed to the Standard Sample Clerk, National Bureau of Standards, Washington 25, D.C.

Thermometric Cells

As part of a continuing program to provide science and industry with temperature standards and measurement methods over a broad range of temperatures, the Bureau issues thermometric cells which utilize the freezing behavior of purified compounds to establish reproducible reference temperatures.

One type of cell, based on highly purified benzoic acid, is suitable for calibrating platinum resistance thermometers. During the past several years, the Bureau has sent many of these cells to educational, governmental, and industrial laboratories throughout this country and to national laboratories or laboratories doing comparable work in several other countries.

The slow freezing of the acid in the cells under prescribed conditions, establishes an equilibrium temperature constant, to within a few ten-thousandths of a degree of the maximum, for at least 2 hr, and reproducible with a standard deviation of 0.0003 °C. The maximum temperature, about 122.360 °C, is certified for each cell with a stated uncertainty of ±0.003 °C. To a large extent, this uncertainty reflects the limitations of assigning values to temperatures between defined points of the International Temperature Scale and does not relate to the constancy with which the temperature is reproduced in a given cell.

The cells are made of glass and are 28 cm long and 51 mm in diameter. An axial thermometer well extends from the top of the cell to about 2 cm from the bottom. At the open end of the well there is sealed an extension 13 cm long which serves as a handle and reduces convection of air in the well. To accommodate thermometers of different sizes, the wells are made with inside diameters of 8, 10, or 12 mm. For the most precise work, the well should provide a close fit to the thermometer being calibrated. However, with suitable precautions for obtaining good thermal contact between thermometer and well and to minimize convection of air in the well, it is possible, for instance, to calibrate satisfactorily a platinum resistance thermometer with an envelope 7 mm in diameter in a cell with well diameter of 10 or 12 mm.

The cells are issued in sets consisting of a certified cell and an uncertified companion cell contained in a wooden instrument case. The companion cell, similar in construction to the certified cell, contains acid of lower purity. It is used in the calibration procedure to preheat the thermometer and the vacuum flask in which the certified cell is placed for measurement.

A complete set of cells in an instrument case may be obtained for $220.00, while replacement cells are available for $155.00 for a certified cell and $40.00 for a companion cell. Orders for cells may be directed to the Pure Substances Section, Analytical and Inorganic Chemistry Division, Rm 137, Bldg 8, National Bureau of Standards, Washington 25, D.C.

Another type of cell which has become available more recently utilizes slow freezing of either phenol (41 °C), napthalene (80 °C), or phthalic anhydride (131 °C) to establish reference temperatures. These glass cells are only 14 cm long and 38 mm in diameter. The thermometer well, 11 cm long and 8 mm inside diameter, is sealed into the top of the cell without an extension.

The cells are primarily intended for the calibration of "solidification point" thermometers. These thermometers are of the liquid-in-glass, partial immersion type, and are used in ASTM testing procedures for basic industrial chemicals. Methods for using the cells in these procedures are being investigated by ASTM committees.

A study of the cells at the Bureau showed the maximum temperature in a cell to be reproducible with a standard deviation of a few ten-thousandths of a degree C as indicated by platinum resistance thermometers and

a few thousandths of a degree as shown by solidification point thermometers. Reflected in the precision with the solidification point thermometers are the difficulties of measuring temperature with this type of themometer. The maximum freezing temperatures in both the phenol and napthalene cells—as indicated by the solidification point thermometers—agree with corresponding temperatures shown by platinum resistance thermometers.

When mercury-in-glass thermometers are being calibrated, an emergent stem correction should be applied to the reading. The magnitude of this correction will depend on the design of the thermometer, the portion of the stem within and outside the cell, the ambient temperature, and the coefficient of expansion of the glass. When a common type of thermometer designed for 8 cm immersion is being used in a phthalic anhydride cell the correction may be about 0.2 °C. The correction will be considerable smaller with the phenol and the napthalene cells, but will be significant if the readings are being made to hundredths or thousandths of a degree.

A report of the results obtained on each cell with both types of thermometers is included with each cell, along with instructions for preparing the cells for measurement.

The napthalene, phenol, and phthalic anhydride cells may be ordered at a cost of $50.00 each from the Pure Substances Section.

PHOTOLYSIS OF ETHANE

THE MECHANISM by which hydrogen atoms are removed from ethane during vacuum ultraviolet photolysis has been determined. Through mass spectrographic analysis of deuterated samples, H. Okabe and J. R. McNesby have shown that two hydrogen atoms are usually split from a single carbon atom to form a hydrogen molecule. The ethylidene produced simultaneously reacts further to form higher hydrocarbons found in the products. This work is part of a basic research program of the Physical Chemistry Division. The program is concerned primarily with the elucidation of elementary processes in chemical kinetics.

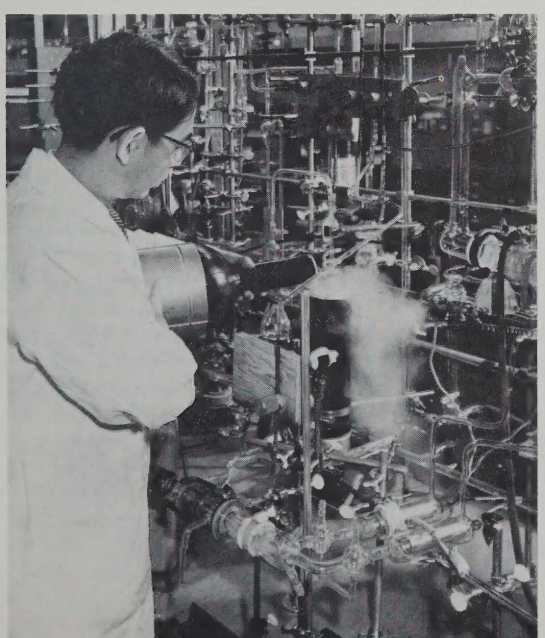
It had previously been believed that ultraviolet photolysis of ethane resulted in the removal of one hydrogen atom from each molecule

$$C_2H_6 \xrightarrow{1470\ A} C_2H_5 + H,$$

or that the ethane molecule was split to form two methyl radicals

$$C_2H_6 \xrightarrow{1470\ A} 2CH_3.$$

By replacing some, or all, of the hydrogen atoms with deuterium, it was possible to determine that the usual action of ultraviolet light is to remove two hydrogen atoms from a single carbon.



To provide the ultraviolet radiation needed for the photolysis of ethane, a water-cooled xenon source was used. This lamp, which contained 20 μ of xenon and 1 mm of neon, produced light having a principal wavelength of 1470 A. A filter was placed between the lamp and the reaction vessel to remove the 1295-A resonance line. Because ordinary glass would not transmit light of the wavelength used, lithium fluoride windows were employed between the lamp, filter, and reaction vessel.

The ultraviolet light from the lamp was passed into partially deuterated ethane (CH_3CD_3), and mixtures of ethane and deuterated ethane (C_2D_6) for various time periods. All runs were made at low ethane pressure and room temperature. Exposure times ranged from 30 sec to 200 min, producing between 0.01 and 2 percent decomposition. After exposure, the fraction of the products volatile at 77 °K was analyzed with a mass spectrometer. In all cases H_2 and D_2 were the dominant hydrogen species detected, with minor amounts of HD being formed (see table). This result leads to the conclusion that two hydrogen atoms must have been stripped from a single carbon atom to produce hydrogen gas and ethylidene (CH_3CH):

$$CH_3CD_3 \xrightarrow{1470\ A} CHCD_3 + H_2,$$

$$CH_3CD_3 \xrightarrow{1470\ A} CH_3CD + D_2.$$

An effect favoring the formation of H_2 over D_2 by a factor of 2 was also noted. The ethylene (C_2H_4) found in the products would result from the isomerization of ethylidene:

$$CHCH_3 \rightarrow CH_2CH_2.$$

The formation of ethylidene leads to the interesting possibility that the reactions subsequent to the re-

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Dr. H. Okabe prepares equipment prior to the photolysis of deuterated ethane. Mass-spectrographic analysis of the products indicates that two hydrogen atoms are removed from a single carbon atom to produce hydrogen gas and ethylidene (CH_3CH). The ethylidene is the basis for higher hydrocarbons found in the products.

Experiment	Ethane pressure		Exposure time	Decomposition [d]	Isotopic analysis hydrogen		
	C_2H_6	C_2D_6			H_2	HD	D_2
	mm Hg		*min*	*Percent*	*Percent*	*Percent*	*Percent*
$C_2H_6-C_2D_6$ mixture							
1	18.7	15.4	200	1.0	69.6	1.9	28.5
2 [a]	19.7	17.7	120	0.8	66.9	1.7	31.3
3 [b]	19.2	13.0	90	.4	73.7	1.6	24.6
4	15.1	20.2	60	.3	58.1	3.3	38.5
5 [c]	16.8	11.0	1	.05	82.0	2.5	15.5
6 [d]	27.8	47.0	0.5	.01	56.3	3.7	40.0
CH_3CD_3							
7	7.5		60	2.0	58.6	16.4	25.0
8	40.8		170	0.3	58.5	16.9	24.6

[a] Methane filter was used to isolate radiation at 1470-A wavelength.
[b] The sample was preirradiated for 2 hr and the noncondensable products at −195 °C were pumped off.
[c] The sample was purified. Traces of ethylene were removed by means of gas chromatography.
[d] Percent decomposition is not strictly related to exposure time since the lamp intensity was not constant from experiment to experiment. The values are based upon ϕ hydrogen=1.

moval of the hydrogen atoms are not controlled by free alkyl radicals, but by carbenes such as ethylidene. One reaction which would produce higher hydrocarbons is that between ethylidene and ethane:

$$CHCH_3+C_2H_6\rightarrow C_4H_{10}.$$

Methane was also found in the reaction products, having been produced by the reaction

$$CH_3CH_3\xrightarrow{1470\ A}CH_4+CH_2.$$

That the methane was formed in this way was demonstrated by the photolysis of CH_3CD_3, in which only CD_3H and CH_3D were formed. The CH_2 probably reacts with ethane to produce propane:

$$CH_2+C_2H_6\rightarrow C_3H_8.$$

These results suggest further experiments on other deuterated hydrocarbons. However, the lack of pure isotopically labeled compounds will require that they be prepared and identified at the Bureau before more results can be obtained. Such a program is being initiated.

[1] *For further details, see* Vacuum UV photolysis of ethane: molecular detachment of hydrogen, *by H. Okabe and J. McNesby, J. Chem. Phys.* (Jan. 1961).

Postdoctoral Research Associateships

THIRTEEN YOUNG SCIENTISTS are now conducting advanced basic studies as Postdoctoral Research Associates at the Bureau. The associateships, sponsored jointly by the National Academy of Sciences-National Research Council and the Bureau, give young scientists an opportunity to pursue a year's study and research in their fields of competence, in close association with a Bureau staff member whose work in the field is well established.

Eleven of the men are pursuing their research projects in Washington, D.C.; the remaining two are at the Boulder, Colo., Laboratories.

The Postdoctoral Resident Research Associateship program, now in its seventh year, is administered by the National Academy of Sciences-National Research Council. The plan provides advanced training in research for creative young scientists who have shown promise of leadership in fundamental research. The Bureau has sponsored the program because it is vitally concerned with the needs of the expanding frontiers of science, and is aware of the necessity for fundamental research in the science of measurement, on which other areas of scientific endeavor and industrial activity are so dependent.

Intensified study and research on the postdoctoral level is traditional among university scientists. The Bureau and the Naval Research Laboratory pioneered in the extension of this practice to government research laboratories. In the intervening years, it has spread to other research and scientific groups and organizations. Not only does such a program provide for the training and development of the best young scientists; it also provides for a "cross-fertilization" of ideas, bringing the benefits of the scientist's new approaches and the results of his research to both organizations—the one at which the research is performed and the one with which the scientist ultimately associates on a permanent basis.

In 6 years of its existence the NBS program has awarded associateships to 44 young men, including the 13 presently at the Bureau. Of the first 31 associates, 14 made application to the Bureau, and were accepted as permanent NBS staff members.

The program at NBS is under the overall direction of the Educational Committee, with actual operation in the hands of a subcommittee composed of Dr. David E. Mann, Chairman; Joseph Hilsenrath; Miss Frankie Keyser; Dr. Pierre J. Ausloos; and Dr. L. M. Kushner.

Applicants for the NRC-NBS Associateships must in all cases have completed the requirements for a doctorate in one of the physical sciences, and must have received their Ph.D. degrees by the time they enter upon the associateship. They also must be United States citizens. Application is made directly to the National Academy of Sciences in response to an announcement, distributed by the Academy annually in November to all universities granting Ph.D. degrees in the physical sciences. Applications are usually closed by February 1 and awards are made April 1. Each applicant indicates, from among the areas of research and the advisors made available, the particular program of research he wishes to pursue, and the staff member under whose guidance this research will be done.

Unless otherwise arranged, the tenure of a research associateship may begin after July 1, and continue for 1 year.

Postdoctoral Research Associates now at the Bureau are:

DR. JOSEPH M. ANTONUCCI, organic chemist—Engaged in research in polymers, particularly high temperature polymers containing fluorine. Advisor: Dr. Leo Wall.

DR. RAYMOND BORKOWSKI, chemist—Investigating primary photochemical processes of organic compounds containing carbonyl in the gas, liquid, and solid phase. Advisor: Dr. Pierre J. Ausloos.

DR. NATHANIEL P. CARLETON, experimental physicist—Investigating the interpretation of observational data in study of optical emission (airglow and aurora). Advisor: Dr. F. E. Roach (Boulder, Colo.).

DR. SOLOMON J. GLASS, physicist—Conducting investigations in the theory of irreversible processes with particular application to electrical conductivity in solids. Advisor: Dr. Arnold H. Kahn.

DR. ROBERT E. LA VILLA, physical chemist—Engaged in research on characteristic energy losses of electrons in metals and alloys. Advisor: Dr. L. Marton.

DR. FREDERICK H. MEIS, chemist—Engaged in theoretical research on energy transfer of collision between atoms and molecules. Advisor: Dr. Kurt E. Shuler.

DR. HARRY L. MORRISON, physicist—Studying quantum statistical mechanics, with emphasis on the participation function of a system of bosons in the neighborhood of the Bose-Einstein transition. Advisor: Dr. Melville Green.

DR. ROBERT S. POWERS, physical chemist—Performing research in effects of plasma sheaths during electron beam-plasma oscillations. Advisor: Dr. J. M. Richardson (Boulder, Colo.).

DR. WALTER L. SADOWSKI, physicist—Performing theoretical investigations in the relationship of the macroscopic irreversibility of thermodynamic processes to the manifest reversibility. Advisor: Dr. Melville Green.

DR. THEODORE N. SARACHMAN, physical chemist—Studying hindered internal rotation and related intramolecular interactions in halogenated derivatives of hydrocarbons by the microwave spectroscopic techniques in use at NBS. Advisor: Dr. David E. Mann.

DR. JAMES F. SCHOOLEY, physicist—Engaged in a cryophysics investigation in paramagnetism, to study the thermal properties of diamagnetic crystals in contact with magnetically cooled paramagnetics. Advisor: Dr. Ernest Ambler.

DR. LOUIS J. STIEFF, physical chemist—Engaged in study of the radiolysis of simple organic compounds, with especial emphasis on free radical reactions occurring in the gas phase. Advisor: Dr. Pierre J. Ausloos.

DR. JEROME WEINSTOCK, physical chemist—Studying the application of quantum and statistical mechanical techniques to the investigation of scattering cross sections between massive particles involving an exchange of charge. Advisor: Dr. Melville Green.

Publications of the National Bureau of Standards

Periodicals

Technical News Bulletin, Volume **45,** No. 2, February 1961. 15 cents. Annual subscription: $1.50, 75 cents additional for foreign mailing. Available on a 1-, 2-, or 3-year subscription basis.

Basic Radio Propagation Predictions for May 1961. Three months in advance. CRPL–D198, issued February 1961. 15 cents. Annual subscription $1.50, 50 cents additional for foreign mailing. Available on a 1-, 2-, or 3-year subscription basis.

Journal of Research of the National Bureau of Standards

Section A. Physics and Chemistry. Issued six times a year. Annual subscription: Domestic, $4; foreign, $4.75.

Section B. Mathematics and Mathematical Physics. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75.

Section C. Engineering and Instrumentation. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75.

Section D. Radio Propagation. Issued six times a year. Annual subscription: Domestic, $4; foreign, $4.75.

Section A. Physics and Chemistry, Volume **65A,** No. 2 March–April 1961.

Mass spectra of some deuteroethanes. E. I. Quinn and F. L. Mohler.

Heats of hydrolysis and formation of potassium borohydride. W. H. Johnson, R. H. Schumm, I. H. Wilson, and E. J. Prosen.

Heat of combustion of borazine $B_3N_3H_6$. M. V. Kilday, W. H. Johnson, and E. J. Prosen.

Thermodynamic properties of thorium dioxide from 298 to 1,200 °K. A. C. Victor and T. B. Douglas.

Calculated energy dissipation distribution in air by fast electrons from a gun source. J. E. Crew.

Vitrons as flow units in alkali silicate binary glasses. L. W. Tilton.

Tetragermanates of strontium, lead, and barium of formula type AB_4O_9. C. R. Robbins and E. M. Levin.

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Section B, Mathematics and Mathematical Physics, Volume **65B**, No. 1, January–March 1961.

On transient solutions of the "baffled piston" problem. F. Oberhettinger.

Special types of partitioned matrices. E. V. Haynsworth.

Bound for the *P*-condition number of matrices with positive roots. P. J. Davis, E. V. Haynsworth, and M. Marcus.

Some computational problems involving integral matrices. O. Taussky.

Computational problems concerning the Hilbert matrix. J. Todd.

Index to the distributions of mathematical statistics. F. A. Haight.

Selected bibliography of statistical literature, 1930 to 1957: IV. Markov chains and stochastic processes. L. S. Deming and D. Gupta.

Nonperiodicals

Climatic charts and data of the radio refractive index for the United States and the world, B. R. Bean, J. D. Horn, and A. M. Ozanich, Jr. NBS Mono. 22 (1960) $2.

Units of weight and measure (United States customary and metric) definitions and tables of equivalents. NBS Misc. Publ. 233 (1960) 40 cents.

Report of the 45th national conference on weights and measures 1960. NBS Misc. Publ. 235 (1960) 75 cents.

Report of the International Commission on radiological units and measurements (ICRU) 1959, NBS Handb. H78 (1961) 65 cents.

Technical Notes

The following Technical Notes are available from the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C. (Order by PB number).

Quarterly radio noise data—June, July, August 1960, W. Q. Crichlow, R. D. Disney, and M. A. Jenkins. NBS TN18–7 (PB151377–7) (1960) $1.75.

VHF radio propagation data for Cedar Rapids-Sterling, Anchorage-Barrow, and Fargo-Churchill test paths April 1951 through June 1958, G. R. Sugar and K. W. Sullivan. NBS TN79 (PB161580) (1960) $4.00.

Bibliography of tropospheric radio wave scattering, R. L. Abbott. NBS TN80 (PB161581) (1960) $2.25.

A survey of spread-*F*, F. N. Glover. NBS TN82 (PB161583) (1960) $1.75.

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A theoretical study of sporadic-*E* structure in the light of radio measurements, K. Tao. NBS TN87 (PB161588) (1961) $1.25.

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Spectrum of ReF_6, J. C. Eisenstein, J. Chem. Phys. **33**, No. 5, 1530–1531 (Nov. 1960).

Publications for which a price is indicated (except for Technical Notes) are available only from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. (foreign postage, one-fourth additional). Reprints from outside journals and the NBS Journal of Research may often be obtained directly from the authors.

Patents

The following U.S. Patents have recently been granted on NBS inventions and, except as noted, are assigned to the United States of America as represented by the Secretary of Commerce.

2,960,652 Nov. 15, 1960. Bridge Method for the Measurement of Core Losses in Ferromagnetic Material at High Flux Densities. William P. Harris and Irvin L. Cooter.

2,961,093 Nov. 22, 1960. Conveyor Belt Sorters. Jacob Rabinow.

2,962,706 Nov. 29, 1960. Aerial Navigation Aid. John R. Hoffman and Robert E. Carlson. (License.)

2,964,703 Dec. 13, 1960. Recording Microwave Hygrometer. Jack Sargent and George Birnbaum.

2,966,864 Jan. 3, 1961. Refrigerator Lock with Inside Release. Elmer R. Weaver.

2,967,894 Jan. 10, 1961. Method for the Preparation of Aromatic Fluorocarbons. Walter J. Plummer, Leo A. Wall, and Roland E. Florin. (Army).

2,968,695 Jan. 17, 1961. System for Monitoring and Controlling the Motion of a Sound Source. Edith L. R. Corliss, Mahlon D. Burkhard, and Walter Koidan.

2,970,278 Jan. 31, 1961. Direct-Coupled Amplifier Construction. John H. Reaves.

2,943,917 Process for the Conversion of Hydrogen. July 5, 1960. Daniel H. Weitzel and William V. Loebenstein. (License.)

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